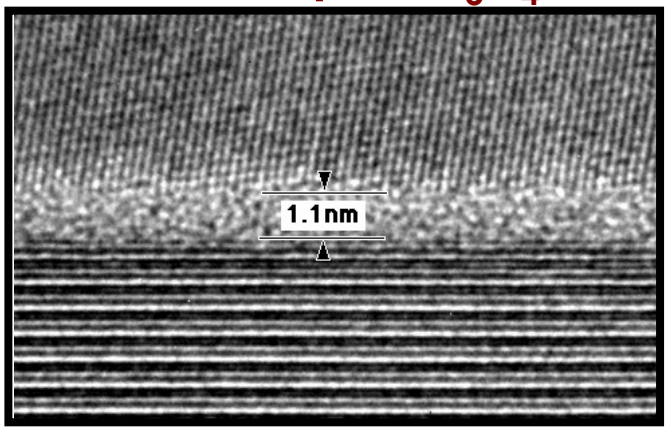
Intergranular and Surface Amorphous Films

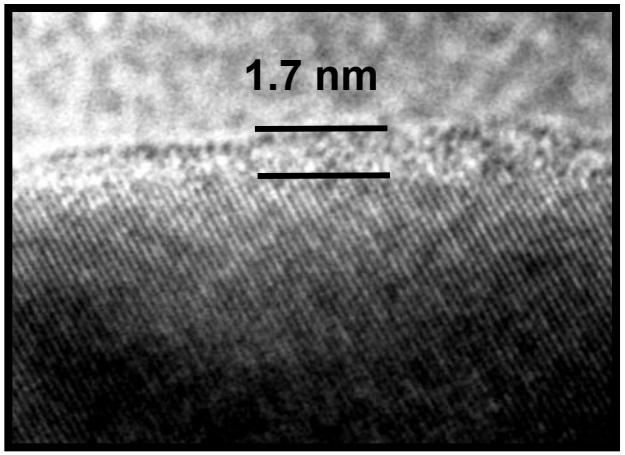
Intergranular and Surficial Films

Ca-doped Si_3N_4



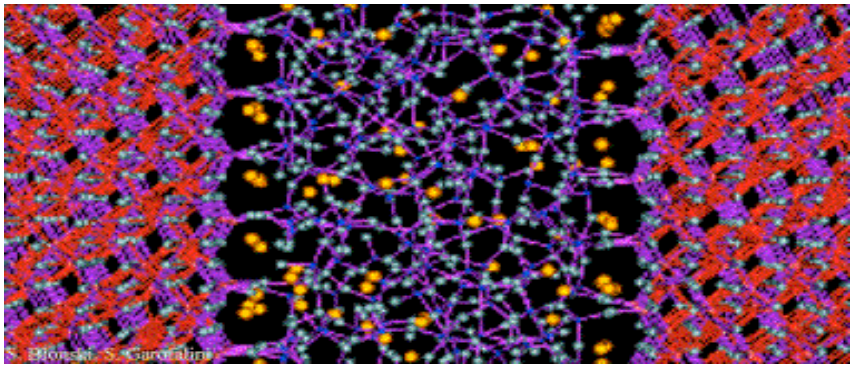
X. Pan (msewww.engin.umich.edu:81/people/panx/Si3N4.html)

YSZ-Si



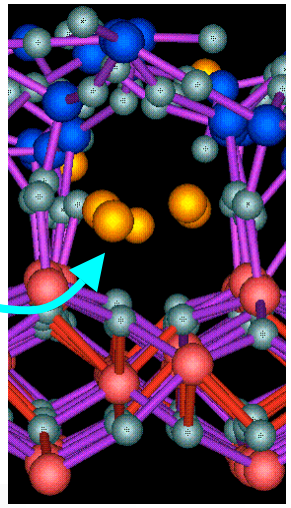
Sung-Yoon Chung (Post-doc), Yet-Ming Chiang (PI), MSE, MIT

(0001)Al_2O_3 with calcium silicate film



Red=Al
Blue=Si
Gray=O
Yellow=Ca

Ca ions in cages



Do such ordered structures form in other materials?

S. Garofalini (PI) Ceram. And Mat. Engineering, Rutgers University

Intergranular films have been observed in many ceramic systems. Y-doped Si_3N_4 samples have been made in Hoffmann's group(Karlsruhe). Some Ca-doped Si_3N_4 are also available.

Stable surficial films with self-selecting thickness and composition, similar to intergranular films, have been observed in several Bi-doped oxides. The films are disordered Bi-Zn-O. The behavior of analogous films on silicon are now being studied under this NSF-EU program.

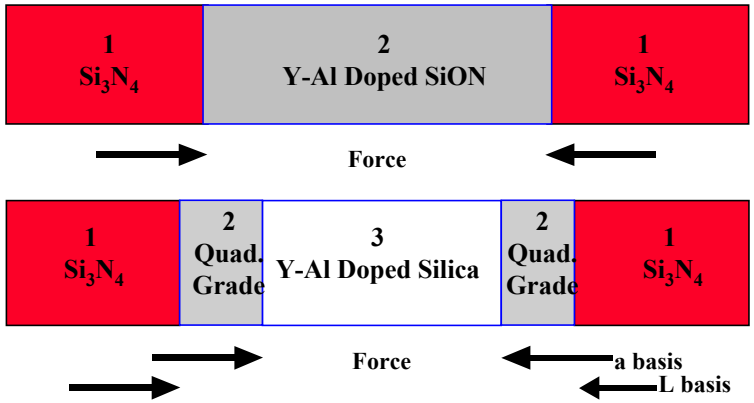
Nano-scale surficial film on YSZ-Si in closed system conditions, 2hrs, 700C. No film is observed on the pure Si control. More experiments need to be done to determine if the films in this system are stable (at equilibrium.)

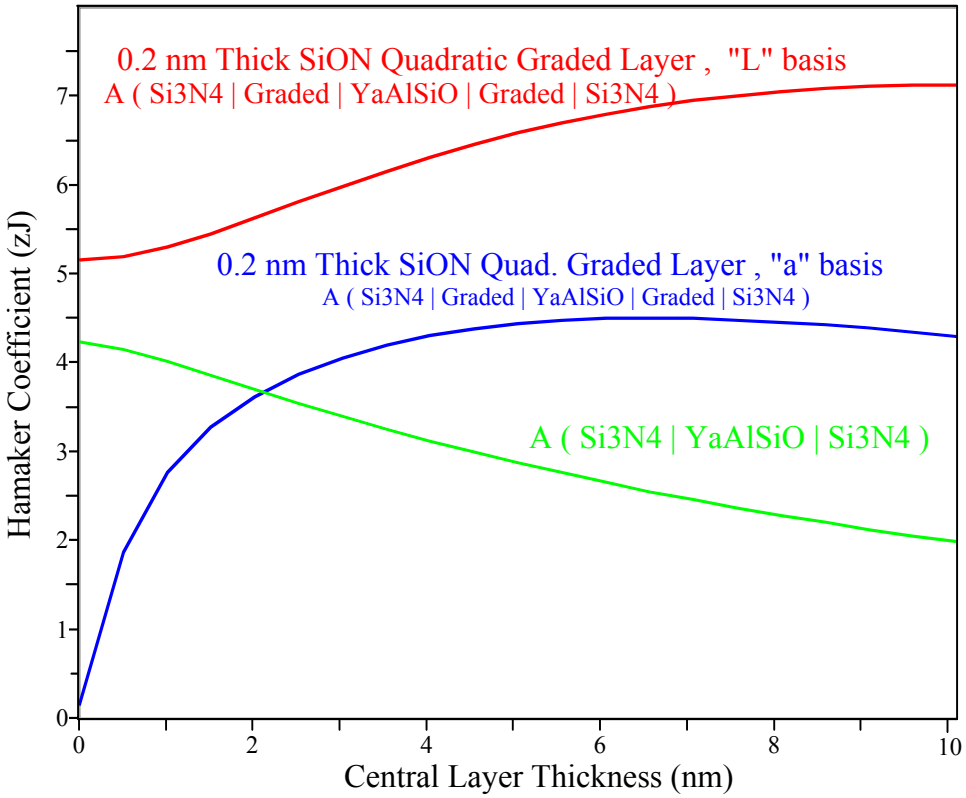
Molecular dynamics simulations are being developed for Si-O films at Si_3N_4 grain boundaries. Previous molecular simulations for Ca-doped Al_2O_3 show an ordered interface caused by adsorption of O ions from the IGF onto under-coordinated Al ions in the Al terminated (0001)Al_2O_3 crystal surface. The Ca ions preferentially go to cage-like structures at under-coordinated O ions at IGF/grain interfaces.

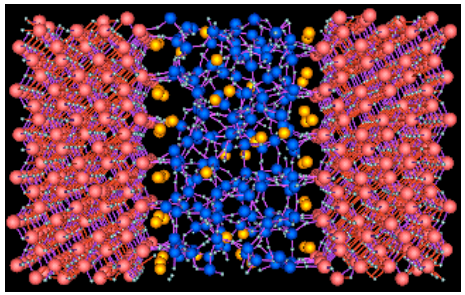
Preliminary results indicate a different behavior in Si_3N_4.

Hamaker Constant for Arbitrary Layers

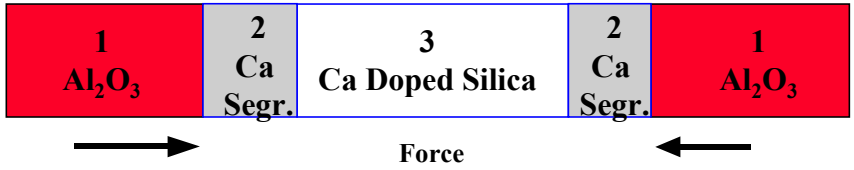
$$E_{interaction} \propto A_{Hamaker}/L^{m}$$







Approximate the structure to calculate $E_{interaction}$



R. H. French (PI) Univ. of Penn. and DuPont Co, L. K. Denoyer, Deconv. & Entropy, V. A. Parsegian, R. Podgornik Nat'l. Inst. of Health

Two grains interact over the thin film between them via virtual photons. This interaction is characterized by the Hamaker constant which depends on the London dispersion spectra for the film material and the grains. A method has been developed to calculate the Hamaker constant for arbitrary layers of materials as a function of thickness. Each layer can have constant or graded (linear or quadratic) material properties. Also, the way the thickness of the "film" is varied can be at constant average composition where all of the layer thicknesses are reduced in proportion, the"L" basis, or the central layer can be reduced in thickness while the other layers remain at constant thickness, the "a" basis.

For a given molecular dynamics equilibrated structure, the Hamaker constant can be calculated for different approximations to the composition profile (linear or quadratic grading of material properties.)

This interaction energy can be included in thermodynamic descriptions of intergranular and surficial films. The phase-field model developed to-date does not include this interaction energy.

Continuum Phase-Field Simulations

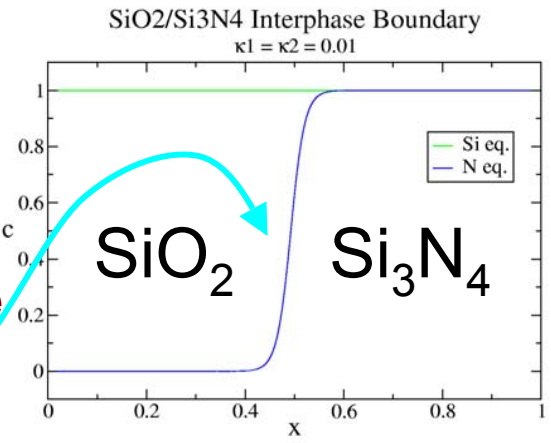
Free Energy Functional

$$F[c_1, c_2, \eta, \theta] = \int_\Omega [f(c_1, c_2, \eta) + 1/2\kappa_1^2 |\nabla c_1|^2 + 1/2\kappa_2^2 |\nabla c_2|^2 + 1/2\nu_0 c_1^2 |\nabla \eta|^2 + s\eta^2 |\nabla \theta| + 1/2\varepsilon^2 |\nabla \theta|^2] dV$$

Homogeneous free energy

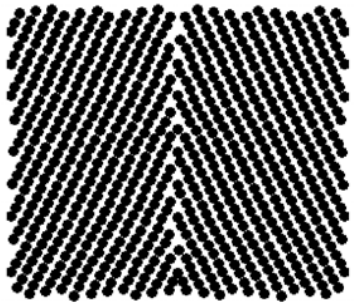
Gradient energy penalty terms

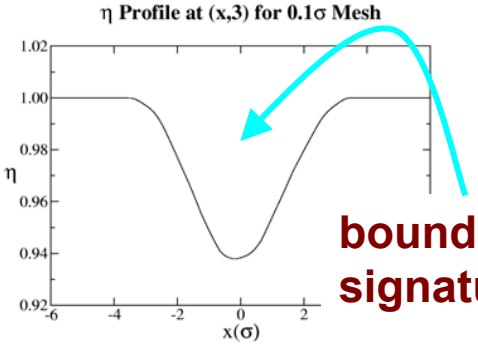
Simple Model Energy



diffuse interface

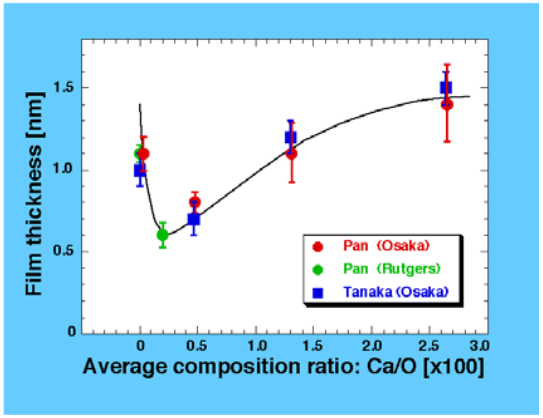
Voronoi Tessellations for Coarse-Graining η





boundary signature

Experimental Results



Continuum description allows stability analysis. Can test model against experimental evidence.

C.M. Bishop (Grad. Stud.) and W.C. Carter (P.I.), MSE, MIT

X. Pan (msewww.engin.umich.edu:81/people/panx/Si3N4.htm

A phase-field model with fields to capture local orientation, θ, a local measure of crystallinity,η, and local composition is being developed,c_i. The free energy functional is developed based on classical thermo and information about interfaces. The gradient energy terms intrinsically incorporate interfacial energies. For neutral compositions reciprocal salt diagrams will be used to reduce the chemical description of the system from 4 to 2 variables. The parameters in the model (underlined in red) will be tuned to molecular dynamics and Monte Carlo simulations and RDF information from nano-volume diffraction experiments. A coarse-graining technique based on Voronoi tessellations is illustrated for a 2-D Lennard-Jones simulation of a tilt boundary. Equilibrium atomistic descriptions of the film are coarse-grained to calculate continuum η, θ and c_i profiles. The parameters in the phase-field model are then varied to match the resulting phase-field interface profiles to those from the atomistic techniques.

The resulting phase-field model can be tested against experimental evidence such as this. The plot shows film thickness against Ca doping in Si_3N_4 with a minimum at a finite thickness. Because of the continuum nature of the model it is straightforward to perform stability analyses like this.